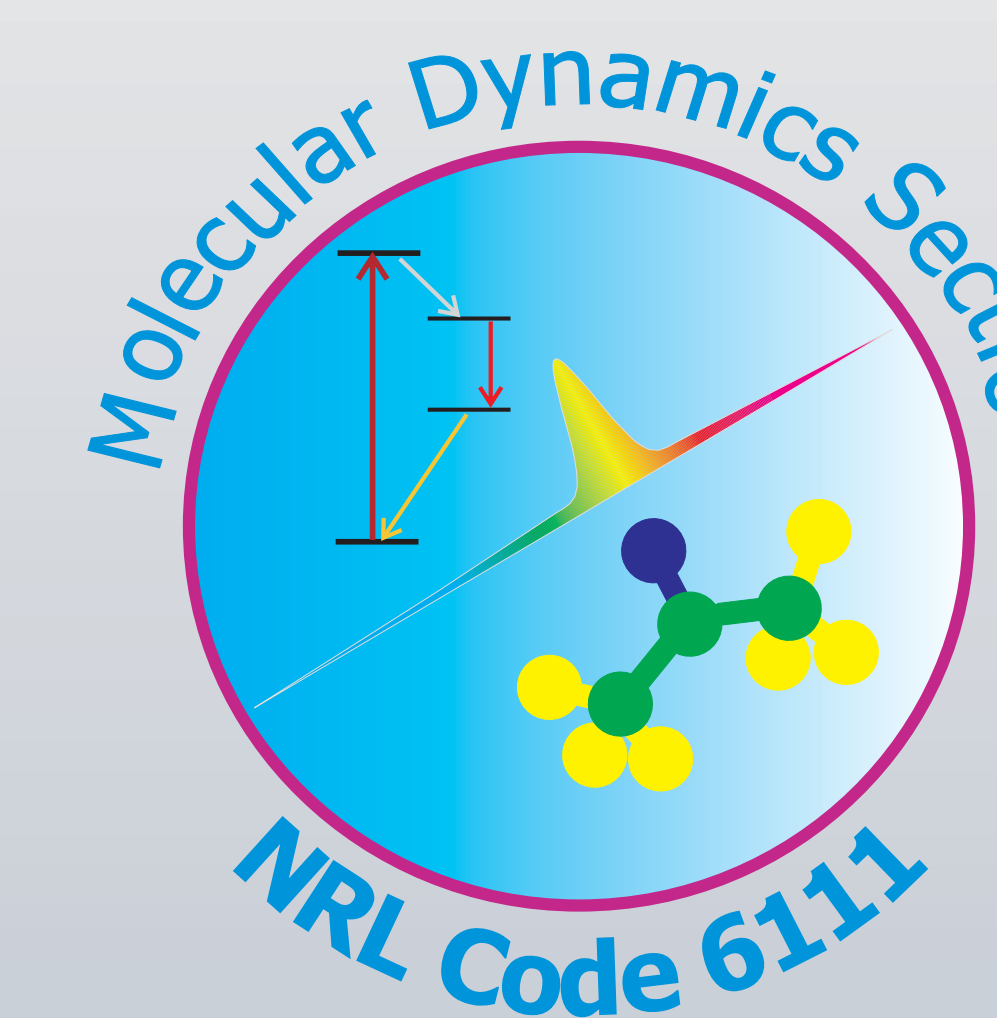# Ultrafast Dissociation Dynamics of Ketones at 195 nm
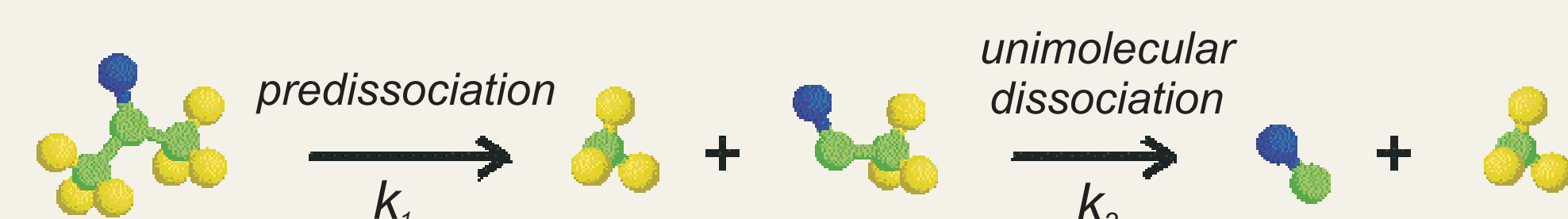
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Molecular Dynamics Section — NRL Code 6111

INTRODUCTION

➤ Photodissociation dynamics of ketones

Multiple dissociation reactions

$$\text{predissociation} \xrightarrow{k_1} \quad + \quad \xrightarrow[\text{dissociation}]{\text{unimolecular}} \xrightarrow{k_2} \quad + $$

Issues: What are the dissociation mechanisms?
Concerted or **stepwise** dissociation?
Energy partitioning among products E_{int}
Dissociation rates k_1 and k_2
Is dissociation statistical? (precludes control)
How do these depend on the details of the specific system?
precursor, excitation wavelength, type of state excited

Model → Product Studies → E_{int} → k_{RRKM}(calc) → ? → k (obs) → Ultrafast Studies
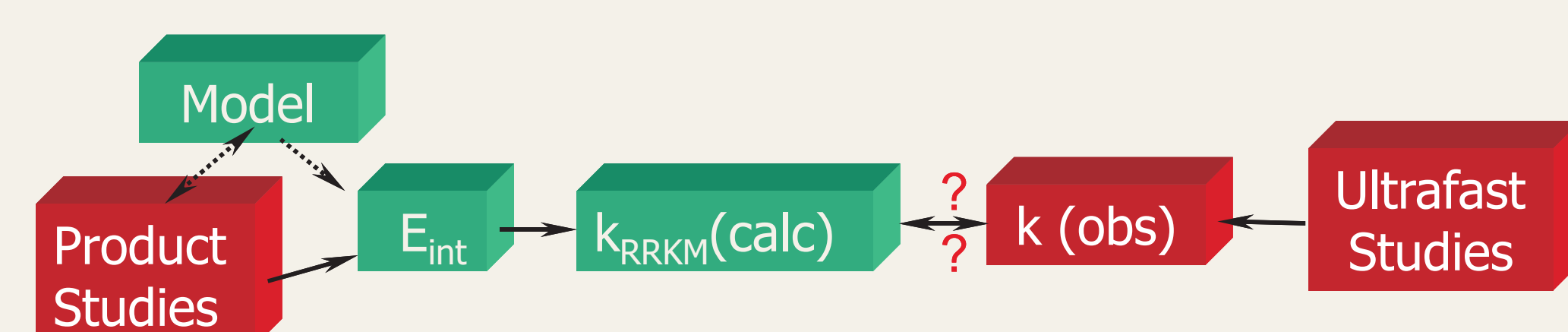
Potential Energy Surfaces for Ketone Photodissociation and Photoionization Detection
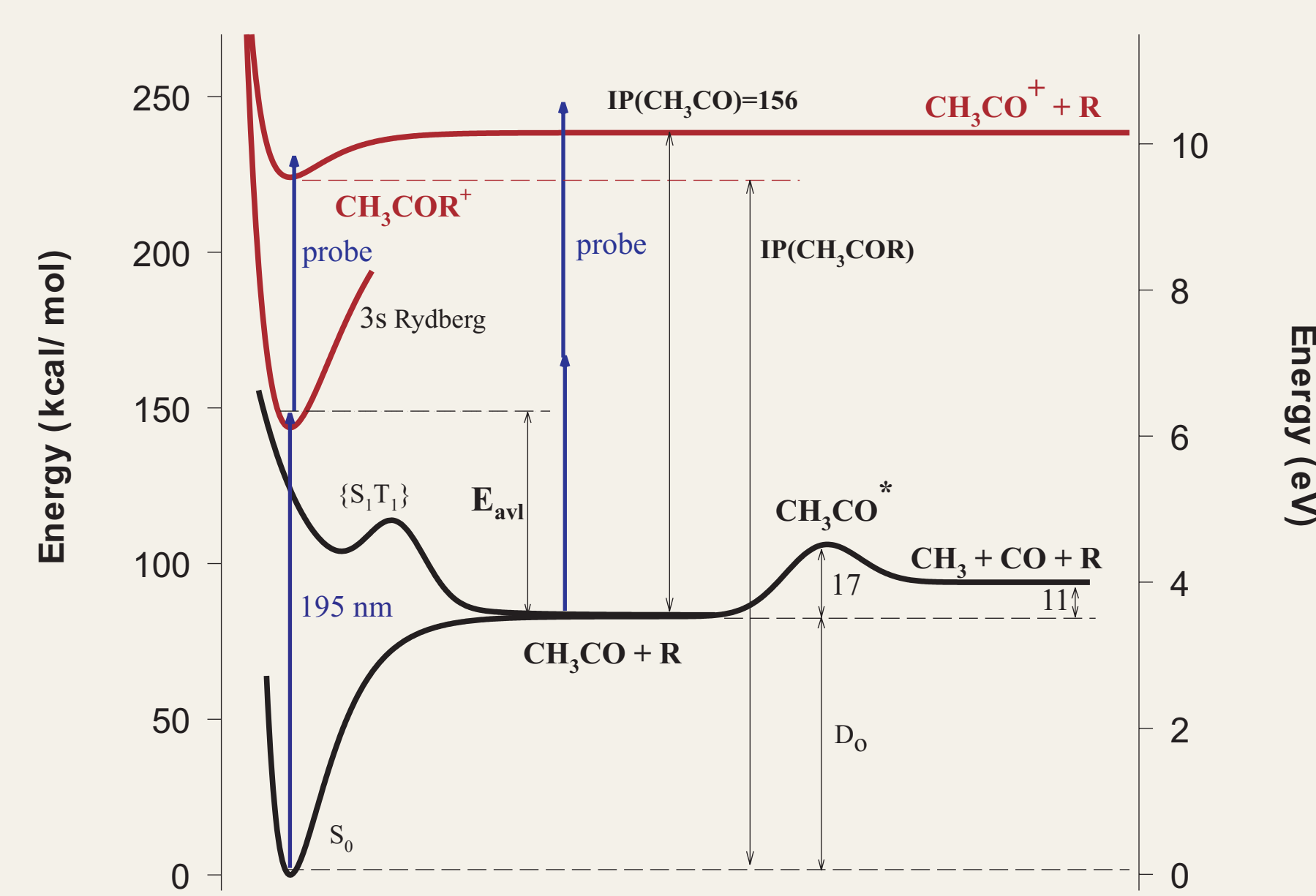
➤ Background

Acetone: "Benchmark" multiple dissociation system
195 nm excitation to 3s Rydberg state[1,2]
Primary dissociation: predissociates via ISC to $\{S_1, T_1\}$ state (4.7 ps)[3,4]
Secondary dissociation: unimolecular dissociation of acetyl intermediate
nonstatistical based on RRKM comparison with E_{int}[3]

Acetyl dissociation - depends on precursor
statistical: acetyl cyanide and acetic acid[5] (E_{int} well determined[6])
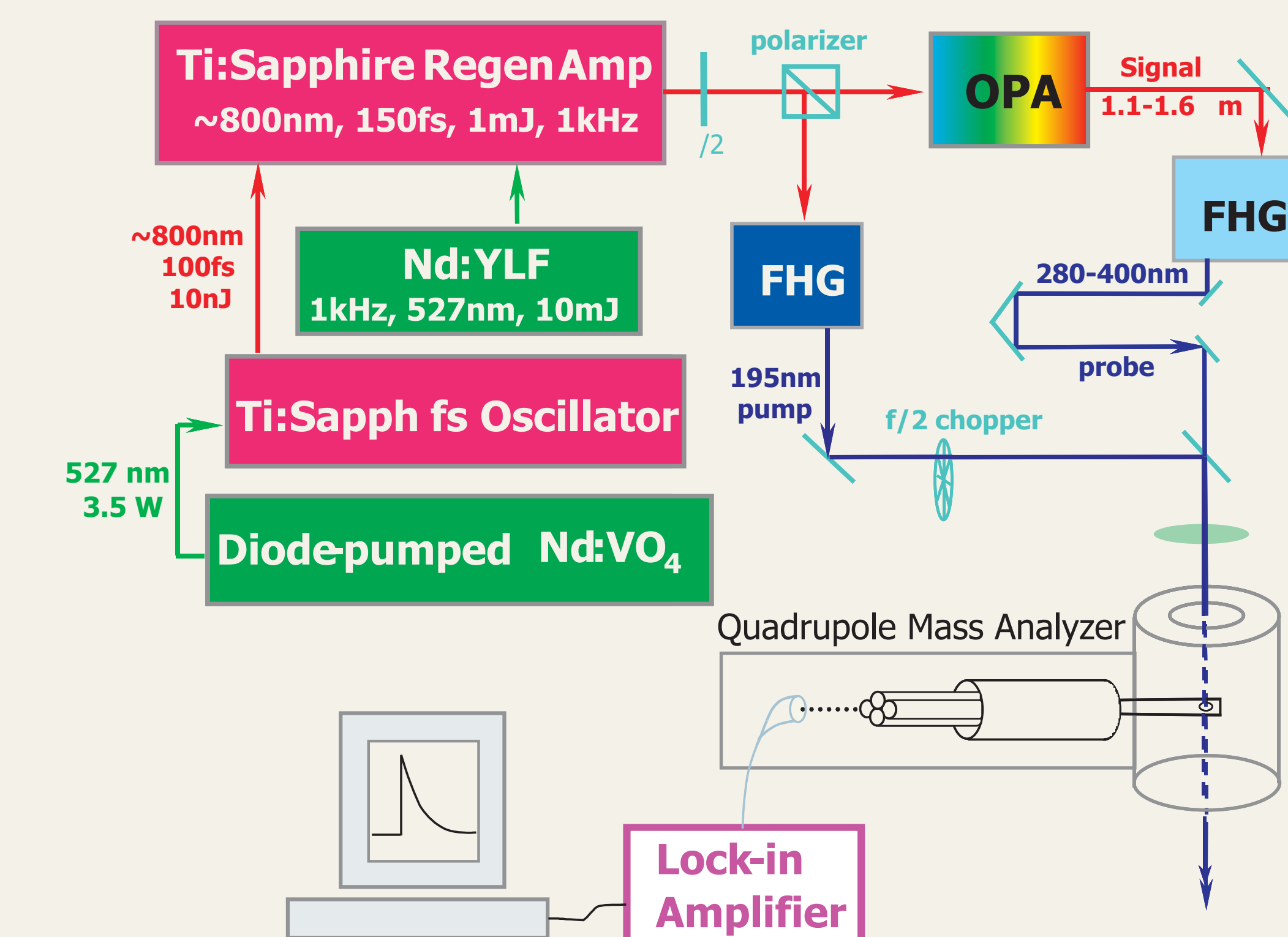nonstatistical: acetone (3s, near 4s)[3,7], acetyl chloride[8]

➤ Current investigations

Photodissociation dynamics for methyl-substitution on acetone
Primary dissociation times measured previously[9]
2-9 ps - similar to acetone
Determine secondary dissociation times
Tunable UV probe with OPA: circumvent dissociative ionization limitation
Little product energy distribution information:
hampers clear assessment of secondary dissociation mechanism
Infer primary partitioning from secondary dissociation rate on
methyl-substitution dependence
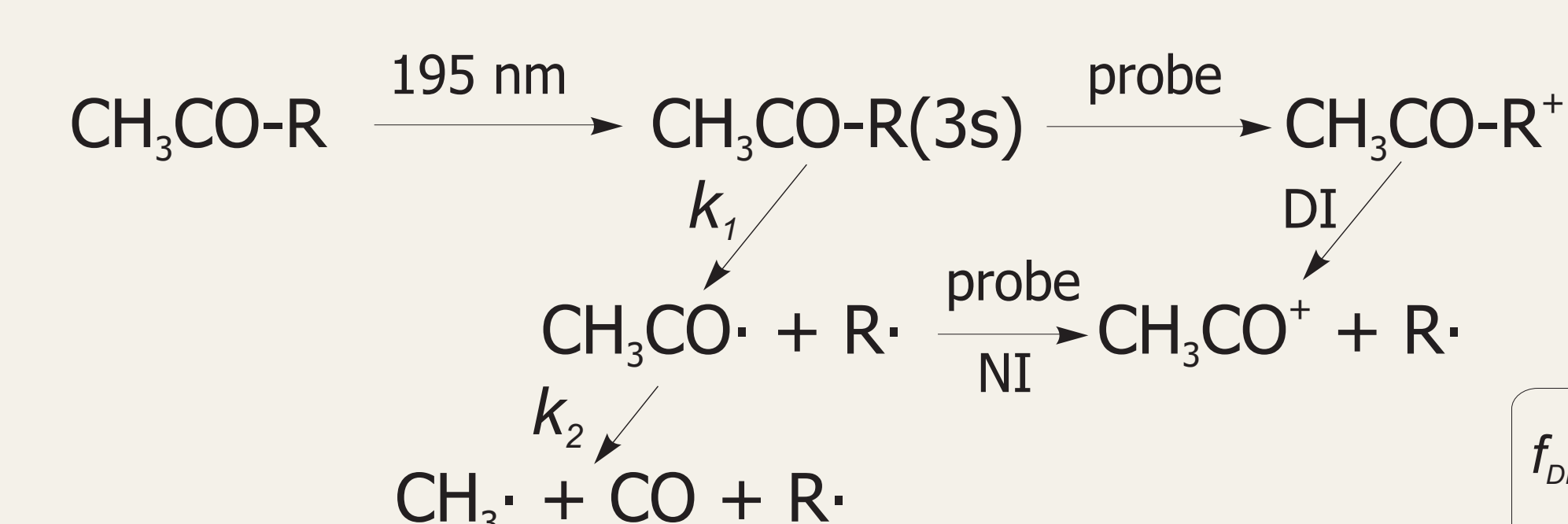Is secondary dissociation of acetyl statistical?

ABSTRACT

The photodissociation dynamics of the 3s Rydberg state of three ketones (CH_3CO-R, R = C_2H_5, C_3H_7, and iso-C_4H_9) and the ensuing dissociation of the nascent acetyl radical following 195 nm excitation were investigated by ultrafast photoionization spectroscopy. The 3s state lifetimes of these ketones are similar (2.5-2.9 ps), though lifetimes of the acetyl radical are 8.6(2) ps for CH_3CO-C_2H_5, 15(3) ps for CH_3CO-C_3H_7, and 23(5) ps for CH_3CO-(iso-C_4H_9), which suggests that for larger R's more vibrational degrees of freedom compete for the excess energy with less energy partitioned into the internal energy of the acetyl radical.

EXPERIMENTAL SETUP

Ti:Sapphire Regen Amp
~800nm, 150fs, 1mJ, 1kHz

Nd:YLF
1kHz, 527nm, 10mJ

Ti:Sapph fs Oscillator

Diode-pumped Nd:VO$_4$

polarizer

OPA — Signal 1.1-1.6 m

FHG

FHG

~800nm 100fs 10nJ

527 nm 3.5 W

280-400nm

195nm pump

probe

f/2 chopper

Quadrupole Mass Analyzer

Lock-in Amplifier

DATA ANALYSIS

Reaction paths of excited ketones:

$$CH_3CO\text{-}R \xrightarrow{195\ nm} CH_3CO\text{-}R(3s) \xrightarrow{probe} CH_3CO\text{-}R^+$$

k_1 : primary rate
k_2 : secondary rate
DI: dissociative ionization
NI: neutral ionization.

$CH_3CO\cdot + R\cdot \xrightarrow[NI]{probe} CH_3CO^+ + R\cdot$
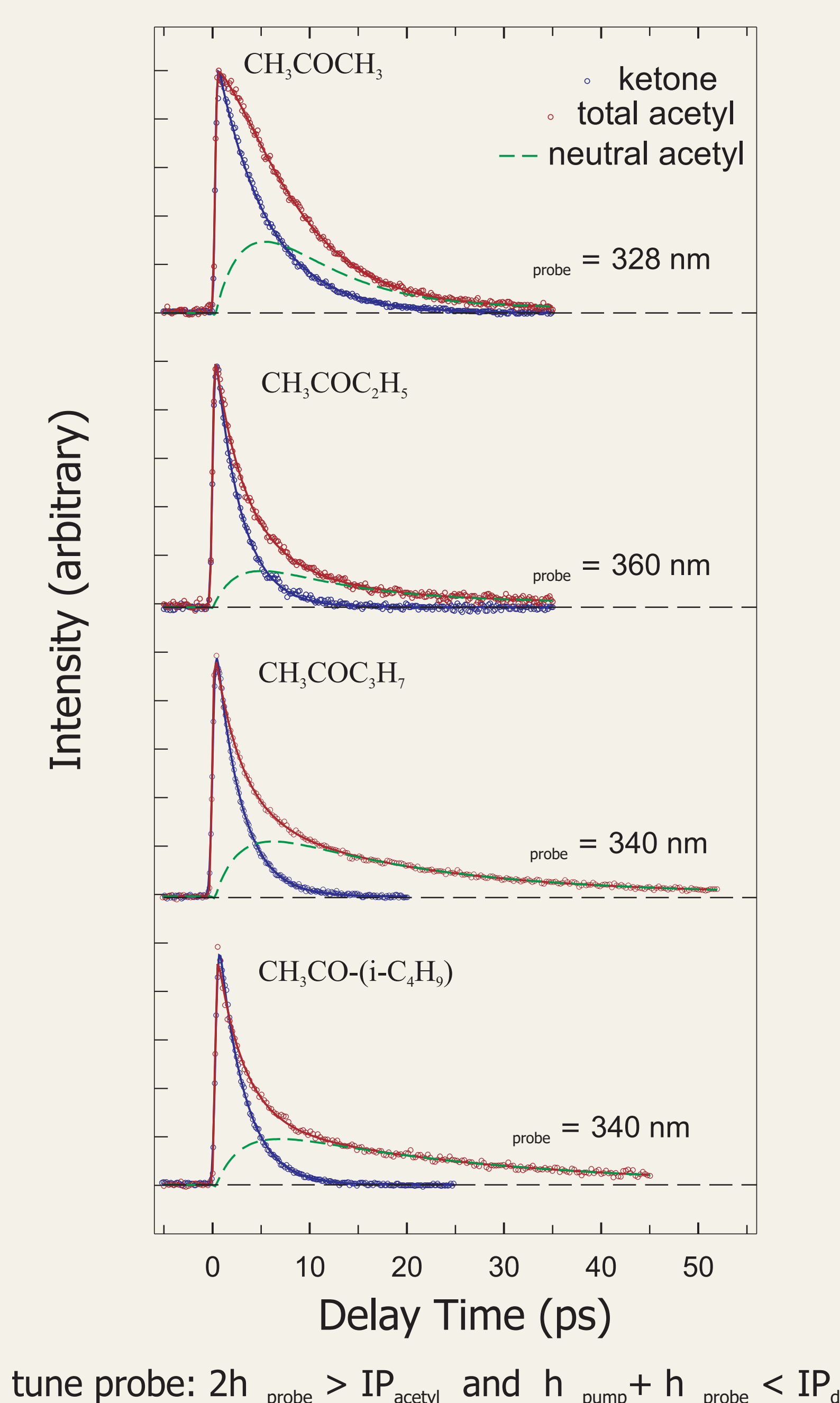
$CH_3\cdot + CO + R\cdot$

f_{DI} : fraction of the acetyl ion due to dissociative ionization
f_{undis} : fraction of the acetyl ion from non-dissociating neutral acetyl
N_2 : Normalization constant

Fit to data:

$$[ketone^+] = N_1 e^{-k_1 t}$$

$$[acetyl^-] = N_2 \{ f_{DI} e^{-k_1 t} + (1 - f_{DI})[(1 - f_{undis}) \frac{k_1}{k_1 - k_2}(e^{-k_1 t} - e^{-k_2 t}) + f_{undis}(1 - e^{-k_1 t})] \}$$

TIME-RESOLVED PHOTOIONIZATION DECAYS

- ketone
- total acetyl
- neutral acetyl

CH_3COCH_3 — probe = 328 nm

$CH_3COC_2H_5$ — probe = 360 nm

$CH_3COC_3H_7$ — probe = 340 nm

CH_3CO-(i-C_4H_9) — probe = 340 nm

Intensity (arbitrary)

Delay Time (ps) — 0 10 20 30 40 50

tune probe: $2h_{probe} > IP_{acetyl}$ and $h_{pump} + h_{probe} < IP_{dis}$

RESULTS SUMMARY

Lifetimes of ketones and acetyl fragments and model predictions of E_{int} of acetyl radicals

CH_3COR	lifetimes (ps)[a]		E_{avl}[b]	E_{int} (kcal/mol)		
R	ketone	acetyl		RRKM[c]	Imp	Stat
CH_3	4.9	4.3	62.1(1.2)	24.2	22.4	31.1
C_2H_5	2.9	8.6	64.0(1.4)	22.6	23.0	23.3
C_3H_7	2.7	15	63.6(1.4)	21.6	22.9	18.2
iso-C_4H_9	2.5	23	63.1(1.5)	21.1	22.7	14.8

a. Uncertainty for parent: ~10%, uncertainty for acetyl: ~20%

b. $E_{avl} = h\nu - D_o$
$D_o = H(CH_3CO) + H(R) - H(CH_3COR)$
$H(CH_3CO)$, $H(R)$, $H(CH_3COR)$ from ref. 10

c. Barrier height = 17 kcal/mol
vibrational frequencies of the acetyl ground state and the transition state from ref. 11

Coincidental ? E_{int} (RRKM) = 75%E^{imp} + 25%E^{stat}

LIMITING CASE MODELS FOR ENERGY PARTITIONING FOLLOWING PRIMARY DISSOCIATION

Impulsive Model[12]

- Assumes ketones break apart due to the excitation of the C-C stretching mode, prior to energy randomization
- Product energy distribution determined by forces from sudden recoil between the two dissociating C atoms

A — O — R
CH_3 — C1 — C2 — C

$$E(A) = E_{avl} \times (C1,C2)/m_{C1} = 0.5 E_{avl}$$
$$E_{int}(A) = E(A) \times (1 - m_{C1}/m_A)$$
$$E_{int}(CH_3CO) = 36\% E_{avl}$$

Statistical Model[13]

- Assumes that IVR occurs much faster than primary dissociation
- The fraction of E_{avl} going into E_{int} of the acetyl radical equals the ratio between the number of vibrational modes in acetyl to the total number of modes in parent molecule
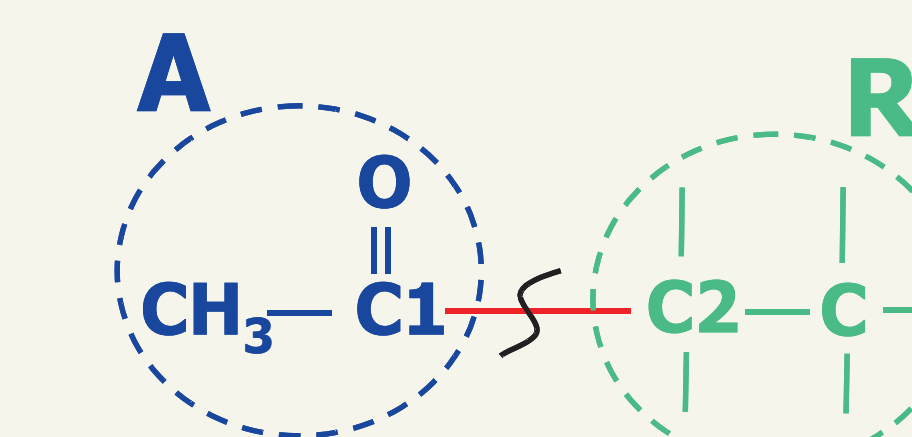
SUMMARY

➤ Single photon excitation to 3s Rydberg state
- primary decay times : ~ 2.5-2.9 ps
similar to the time scale of acetone

➤ Secondary dissociation of acetyl
- tunable UV probe : reduce dissociative ionization
- decay times increase as R gets larger
- little undissociated acetyl observed

➤ Interpretation by comparison with models:
- no independent information on product energy distribution: E_{int} (acetyl) not known
- knowledge of primary and secondary decay rates not enough to establish the dissociation mechanism
- compare observed rate with model predictions
E_{int} from limiting case model prediction: impulsive/statistical
E_{int} inferred from RRKM with observed decay rate
• impulsive model agrees better with RRKM inferred E_{int}
• statistical model predicts the trend
• fixed fraction of impulsive and statistical reservoirs agree with RRKM inferred E_{int}

➤ Complementary information from product energy analysis and theoretical calculations needed to obtain a more comprehensive picture

References

1. G. A. Gaines et al, J. Phys. Chem. 92 (1988) 2762; D. J. Donaldson et al, J. Phys. Chem. 92 (1988) 2766.
2. H. Zukerman et al, J. Phys. Chem. 92 (1988) 4835.
3. J. C. Owrutsky et al, J. Chem. Phys. 108 (1998) 6652; ibid. 110 (1999) 11206.
4. S. W. North et al, J. Chem. Phys. 102 (1995) 4447.
5. J. C. Owrutsky et al, J. Chem. Phys. 111 (1999) 7329.
6. S. W. North et al, J. Phys. Chem. A 101 (1997) 9224; R. J. Horwitz et al, J. Phys. Chem. 101 (1997) 1231; S. S. Hunnicutt et al, J. Phys. Chem. 95 (1991) 562; D. R. Peterman et al, Chem. Phys. Lett. 236 (1995) 564.
7. S. K. Kim et al, J. Phys. Chem. 103 (1995) 477; S. K. Kim et al, Chem. Phys. Lett. 250 (1996) 279.
8. T. Shibata et al, J. Phys. Chem. A 102 (1998) 3643.
9. A. P. Baronavski et al, Chem. Phys. Lett. 333 (2001) 36.
10. NIST Chemistry WebBook: http://webbook.nist.gov.
11. S. Deshmukh et al, J. Phys. Chem. 98 (1994) 12535.
12. K. A. Trentelman et al, J. Chem. Phys. 91 (1989) 7498.
13. R. J. Campbell et al, J. Am. Chem. Soc. 89 (1967) 5103.

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